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NMR, DSC, and Electrical Conductivity Studies
of MEEP Complexed with NaCF_3SO_3 .

by

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NMR, DSC, AND ELECTRICAL CONDUCTIVITY STUDIES OF MEEP
COMPLEXED WITH NaCF_3SO_3

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ABSTRACT

^{23}Na NMR, electrical conductivity, and DSC studies have been carried out on MEEP complexed with NaCF_3SO_3 . All results are similar to those for other amorphous ion conducting polymers. Specifically, the NMR spectrum associated with mobile Na^+ ions exhibits motional narrowing above the glass transition temperature, and activation energies deduced from both T_1 and linewidth measurements reflect localized motion of the cations. The electrical conductivity exhibits the usual non-Arrhenius behavior. However, using previous data for PDMS-EO complexes, it is shown that the VTF or WLF equations are only approximate as the parameters depend upon the temperature range. This sheds light on several discrepancies in the literature.

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1. Introduction

In recent papers, the authors have reported nuclear magnetic resonance (NMR), electrical conductivity, and differential scanning calorimetry studies (DSC) on poly(propylene oxide) (PPO) [1,2] and poly(dimethylsiloxane-ethylene oxide) (PDMS EO) [3,4] complexed with sodium salts. In the present note, the work is extended to poly(bis-methoxyethoxyethoxide) phosphazene (MEEP) complexed with alkali metal salts. The motivation for the work is that MEEP exhibits a rather high ionic conductivity at room temperature [5-7] and thus is of interest as a solid electrolyte.

2. Experiment and Data Reduction

The MEEP was dried in vacuum for 48 hours at 110°C prior to use. It was dissolved in tetrahydrofuran in a teflon cup and sodium triflate was added while stirring. The concentration was one sodium ion per four polymer repeat units. For the electrical measurements the sample was loaded into a shielded cavity which was then attached to the cold finger of a Precision Cryogenics CT-14 dewar. All procedures, including loading of the DSC pans and NMR sample tube were carried out in a dry box with a relative humidity of less than 5%.

All remaining techniques for making the electrical, NMR, and DSC measurements are the same as described elsewhere [3]. In the case of the electrical conductivity, a different data analysis technique was applied since the cell did not lend itself well to geometric data reduction. Instead, the dielectric constant at 77K was set equal to 5 with subsequent scaling of the imaginary part of the dielectric constant and ultimately the electrical conductivity. Consequently, there is some uncertainty associated with the absolute value of the electrical conductivity. However, the precision of the data is quite good, probably better than 1%, and since the results are only uncertain by some multiplicative factor, the values of T_0 and E_a determined as described below remain reliable.

3. Results and Discussion

3.1. DSC

The results of the DSC measurements are shown in fig. 1. For the uncomplexed MEEP the onset, central, and end of the glass transition occur at -82 , -78 , and -73°C , respectively. As expected, the corresponding values for $\text{MEEP}_4\text{:NaCF}_3\text{SO}_3$ are higher, -61 , -54 , and -47°C , respectively. The increase in the glass transition temperature in PPO, for example, with the addition of salt is a well known phenomenon [8].

3.2. NMR

The ^{23}Na NMR results are qualitatively similar to those obtained for a variety of amorphous polymer - sodium salt complexes. [1-4] As in the other materials two distinct spectral responses were observed, one associated with mobile Na^+ and the other with a bound Na configuration. The mobile resonance is characterized by spin lattice relaxation times (T_1) that are typically two or three orders of magnitude shorter than the bound resonance T_1 . Only small quantities (less than $\sim 5\%$) of the nuclei giving rise to the total signal could be identified with the bound Na at any given temperature throughout the range of measurement ($133\text{-}371\text{K}$). Thus no attempt was made to determine the relative concentrations of bound and mobile Na as a function of temperature, as had previously been done for PDMS/EO [3] and PPO [2] complexes.

Figure 2 is an Arrhenius plot of T_1 , for the mobile Na resonance obtained at an operating frequency of 81 MHz. The relatively small T_1 values (<10 ms) which occur even below T_g suggest the presence of short range ion motion. These motions may be associated with hopping within a frozen lattice, [9] although it is well recognized that the rate determining process for ionic conductivity involves segmental motion of the polymer above T_g . The presence of a T_1 minimum in the vicinity of 318 K is clear from the data, and the roughly linear region between 213 and 306 K indicates an activation energy of approximately 0.27 eV. Similar T_1 behavior has been observed in a PDMS/EO - NaCF_3COO complex [4].

Figure 3 represents an Arrhenius plot of $(T_2^*)^{-1}$, the reciprocal of the free induction decay constant, where $(\Delta T_2^*)^{-1}$ is approximately equal to the full-width-at-half-maximum linewidth. As observed in all other sodium salt-polymer complexes studied in this laboratory, [1-4] the ^{23}Na resonance (associated with the mobile cation) begins to narrow just above the central T_g . The linear region between 223 and 268 K implies an activation energy of about 0.20eV. The activation energies inferred from the T_1 and T_2^* data are considerably smaller (by nearly an order of magnitude) than the value that would be obtained in attempting to fit the conductivity to an Arrhenius relationship by neglecting the curvature of the data points. Again this indicates that local motions are primarily responsible for both spin-lattice relaxation and resonance line narrowing. The T_1 mechanism is most probably mediated by the interaction between the ^{23}Na quadrupole moment and fluctuations of the surrounding electric field gradient whereas T_2^* is influenced by both the quadrupole interaction and dipolar interactions, as it has been observed that the spin-spin relaxation time, T_2 (determined from spin-echo measurements) also exhibits an increase in the region of the motional narrowing. From the data in Figure 3, it can be seen that the resonance begins to broaden above 278K. This is apparently a result of lifetime broadening as T_1 reaches values of only several hundred microseconds in this temperature region.

3.3. Electrical Conductivity

The results of the electrical conductivity studies for the complexed material are shown in fig. 4. The electrical conductivity for the uncomplexed MEEP was too low to be measured in the cell used in the present work. The curvature which is often observed for non-crystalline ion containing polymers is apparent. Consequently, the VTF equation [10] in the form:

$$\sigma = AT^{-1/2} \exp\{-E_a/k(T-T_0)\} \quad (1)$$

was best-fit to the data using techniques described in detail elsewhere [4]. The values of the fitting parameters were determined to be $E_a=0.0848$ eV (8.18 kJ/mol), $T_0=175.3$ K, and $\log_{10}A=+0.25$ and the RMS deviation in $\log_{10} \sigma$ was 0.049.

The strong curvature resolves one point concerning MEEP. Namely, previous workers [6,7] were unable to distinguish between Arrhenius and VTF behavior though shallow curvature was reported. The reason, of course, is that those authors did not extend their work to low enough temperatures as they were confined to the region above 270K. The present work makes it clear that MEEP exhibits VTF behavior as do other amorphous polymers such as PPO [1,2,10,11] or PDMS-EO [3,4,12].

Further, the value of T_0 is found to be 44°C below the "central" T_g as determined by DSC. This is similar to previous results for PPO [1,2] and PDMS-EO [3,4] obtained by the authors. The present value of T_0 is somewhat higher than the values of Tonge and Shriver [7] who fit both eq. (1) and an Arrhenius expression to their data. Those authors find values of $T_g - T_0$ from 50 to 120K. (The values of T_g quoted by Tonge and Shriver are several degrees lower than the "central" T_g 's of the present work and thus the values to be compared with 44K of the present work are probably about 60-120K.)

This discrepancy can be explained at least in part by the difference in temperature range between the two experiments. To show this, the data from ref. 4 has been reanalyzed using eq. (1) over various temperature ranges. The data of the present work were not used because of the limited temperature range involved. The comparison is probably quite good because the T_0 's are similar, being 175K in the present work for MEEP and 176K for PDMS-EO [4]. The results are listed in Table 1. It is seen that when the data below 300K are eliminated, the values of T_0 begin to decrease rapidly along with a corresponding increase in E_a . Consequently, data whose range begins far above T_g are expected to exhibit a low value of T_0 as is the case for the results of Tonge and Shriver.

This, of course, points out the approximate nature of the VTF equation. Specifically, it shows that the data is more Arrhenius at high temperatures than is allowed by the VTF equation. A similar observation has been reported recently by Giles [14] for amorphous phosphate ester extended and crosslinked poly(ethylene glycol) complexed with LiCF_3SO_3 .

It is also apparent from Table 1 that if only a few of the lowest temperature data points are eliminated, the values of T_0 are higher than expected. This accounts, at least in part, for a previously noted discrepancy in comparing our results for PDMS-EO [3,4] with those of Bouridah et. al. [13]. Specifically, T_0 is lower and E_a is larger than those parameters reported by the latter group, whose data began at about 295K.

It is of interest to investigate this effect more closely. Both low and high temperature data from ref. 4 were eliminated and eq. (1) was best fit to the data. Those results are also listed in Table 1. A very strong increase in the value of T_0 is accompanied by a strong decrease in E_a . Consequently, this shows that intermediate temperature range data will exhibit large values of T_0 and small values of E_a .

It is important to note that this effect causes E_a to always decrease when T_0 increases. Consequently, this behavior cannot account for the variation of T_0 and E_a with pressure, for example, which has recently been reported [12]. The reason is that it was found that both E_a and T_0 increase as pressure increases [12]. Of course, as eq. (1) was fit to the data over different temperature ranges, the actual values will be affected somewhat.

In order to further emphasize the approximate nature of the VTF or WLF equations, it is pointed out that Nozaki and Mashimo have recently reported very low frequency dielectric relaxation data in poly(vinyl acetate) and showed that the relaxation time exhibits Arrhenius behavior below T_g [15]. This is consistent with the recent comments of Giles [14].

Finally, for completeness, the VTF equation in the form:

$$\sigma = A' \exp\{-E_a'/k(T-T_0')\} \quad (2)$$

was best-fit to the data and the resulting fitting parameters were $\log_{10}A' = -1.09$, $E_a' = 0.082$ eV, and $T_0' = 176.3$ K. In addition, the mathematically equivalent WLF equation [16]

$$\log_{10}(\sigma(T)/\sigma(T_g)) = C_1(T-T_g)/(C_2+T-T_g) \quad (3)$$

was best-fit to the data with the resultant fitting parameters given in Table 2. The WLF parameters are similar to those reported for other amorphous materials [1,3,4,12].

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Table 1. Best fit VTF parameters for PDMS-EO using the data of ref. 4.

Temperature Range	$\log_{10} A$ ($\Omega\text{-cm}$) ⁻¹	E_a (eV)	T_o (K)	RMS Deviation
250-380	-0.50	0.103	176.4	0.0096
260-380	-0.57	0.099	178.9	0.0069
270-380	-0.61	0.097	180.2	0.0063
280-380	-0.62	0.097	180.7	0.0062
290-380	-0.66	0.094	182.4	0.0060
300-380	-0.64	0.095	181.8	0.0063
310-380	-0.54	0.102	176.1	0.0064
320-380	-0.23	0.125	157.7	0.0057
250-340	-0.37	0.108	173.9	0.0067
255-340	-0.42	0.106	175.3	0.0056
260-340	-0.48	0.103	176.8	0.0046
265-340	-0.53	0.101	178.3	0.0039
270-340	-0.52	0.101	178.0	0.0040
275-340	-0.56	0.099	179.4	0.0038
280-340	-0.51	0.102	177.5	0.0035
285-340	-0.64	0.095	182.1	0.0017
290-340	-0.65	0.094	182.7	0.0018
295-340	-0.71	0.091	184.8	0.0016
300-340	-0.79	0.087	188.4	0.0013
305-340	-0.90	0.081	192.7	0.0010
310-340	-0.99	0.076	196.5	0.0009
315-340	-1.16	0.067	204.5	0.0003

Table 2. DSC results and best fit WLF parameters for MEEP₄NaCF₃SO₃.

	T_g (K)	C_1	C_2 (K)	$\log_{10} \sigma(T_g)(\Omega\text{-cm})^{-1}$	RMS Deviation
Onset	212	11.5	35.7	-12.6	0.048
Central	219	9.6	42.7	-10.7	0.048
End	226	8.3	49.7	-9.4	0.048

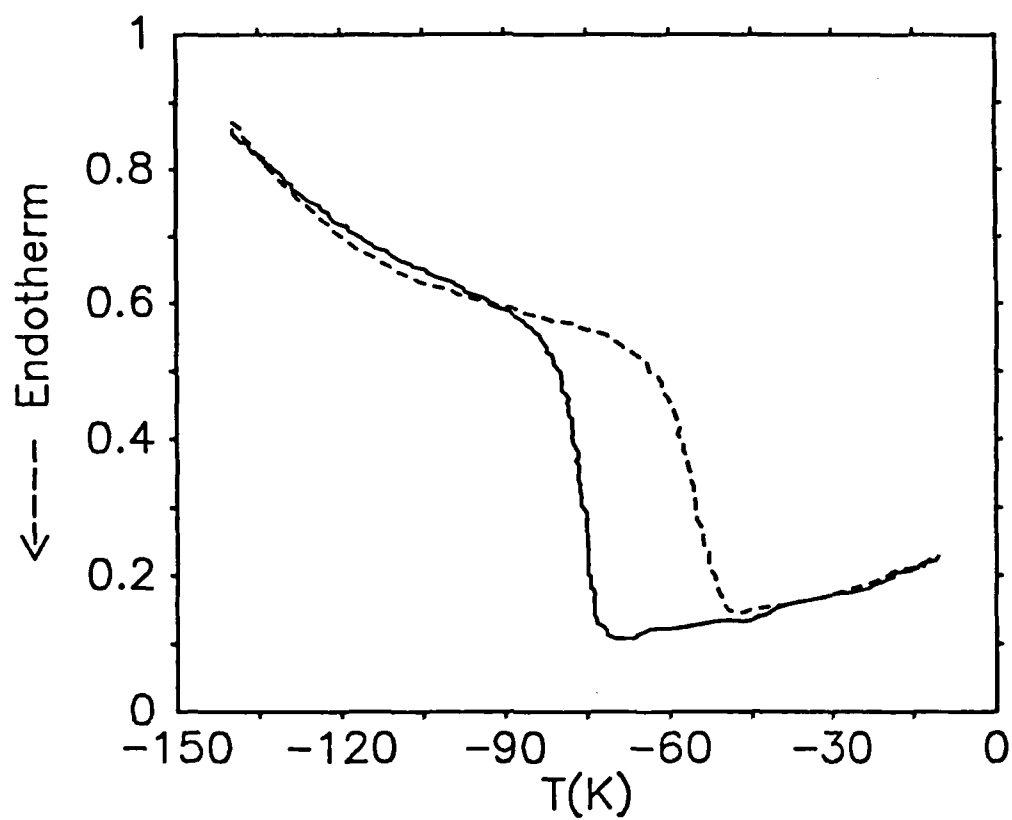


Figure 1. DSC thermogram for (a) uncomplexed MEEP-solid line and (b) MEEP₄NaCF₃SO₃-dotted line. The data were taken at 10 K/min.

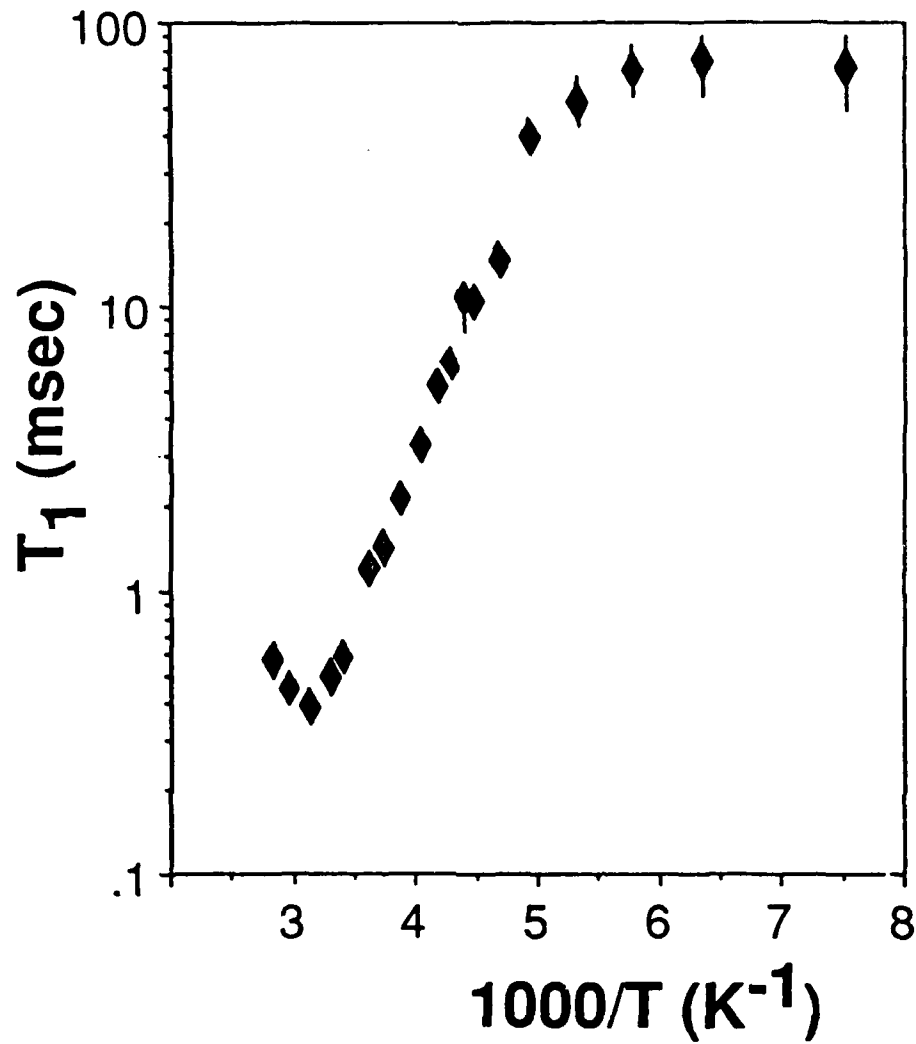


Figure 2. Arrhenius plot of the ^{23}Na spin-lattice relaxation time in $\text{MEEP}_4\text{NaCF}_3\text{SO}_3$. The spectrometer frequency is 81 MHz and the T_1 minimum occurs at about 318K.

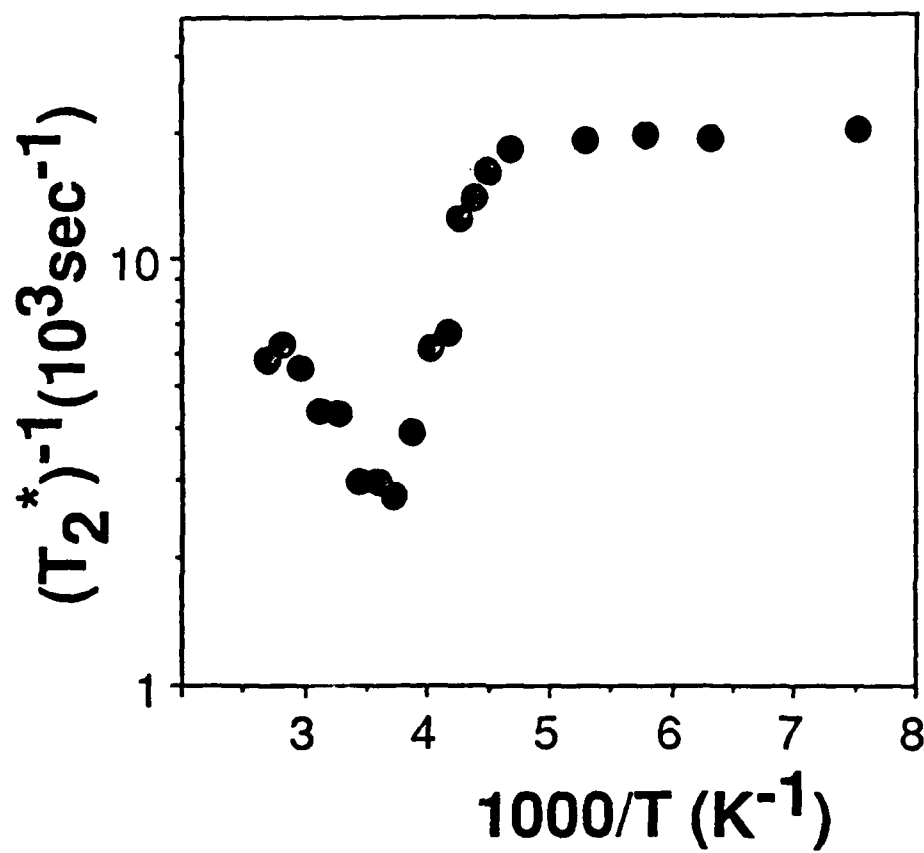


Figure 3. Arrhenius plot of the inverse ^{23}Na free induction decay constant, $(T_2^*)^{-1}$, in $\text{MEEP}_4\text{NaCF}_3\text{SO}_3$.

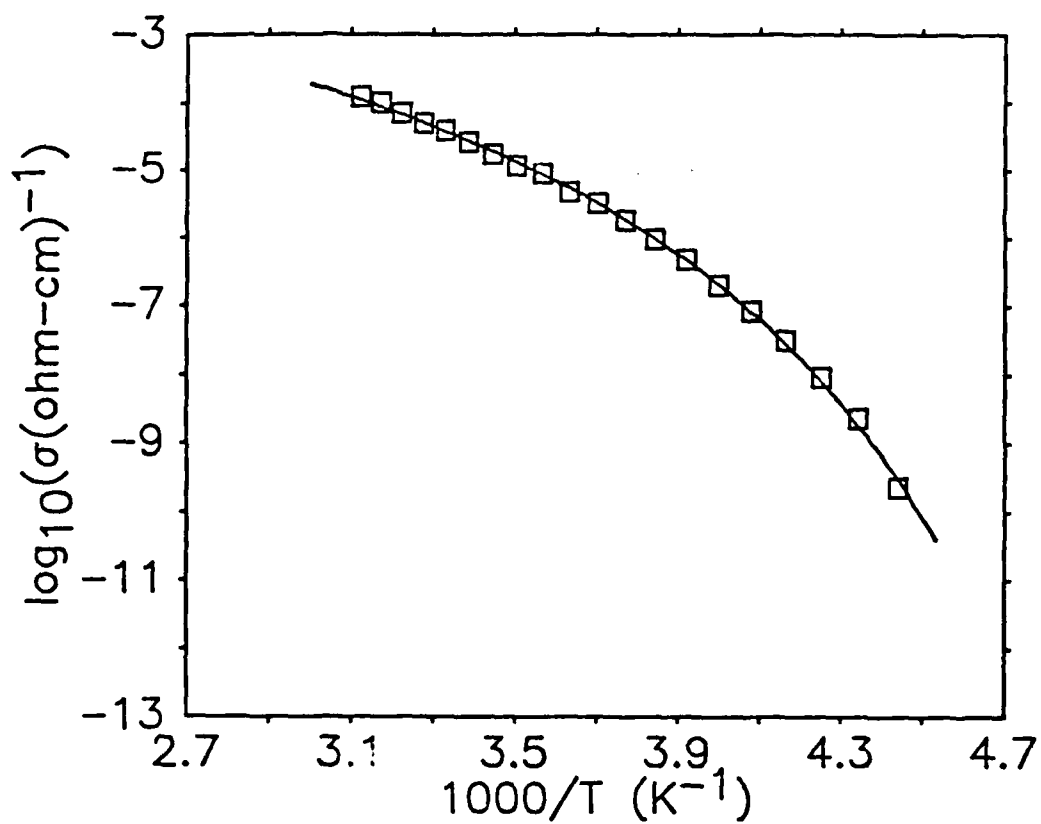


Figure 4. Arrhenius plot of the electrical conductivity data for $\text{MEPP}_4\text{NaCF}_3\text{SO}_3$. The solid line is the best fit VTF equation (eq. 1).

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